

SEPARATION OF BUTADIENE BUTENE MIXTURE WITH MIXTURES OF
AMMONIA AND ETHYLENE IN NEAR CRITICAL CONDITIONS

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Abstract

We describe the results of an investigation into the separation of mixtures of 1,3-butadiene and 1-butene conducted at near critical conditions. Selected solvents and solvents containing ammonia as an entrainer are compared with respect to their selectivity in removing 1-butene from this close boiling mixture. Separation factors of 1.4 to 1.8 at a pressure of 600 psig and a temperature of 20 C are observed for mixtures containing 5%-8% ammonia in ethylene. Pure solvent gases, on the other hand, such as ethane, ethylene, and carbon dioxide show no selectivity. This is also true for ethane /ammonia mixtures which also appear poor as separating agents for this mixture. Experimental results are compared with values predicted by a modified two parameter corresponding states equation with reasonably good agreement. A case is made for the choice of an entraining component to be made on the basis that it contributes a chemical property to the system enabling the same selection criteria described by Elgin to be used in SC processes as are in liquid-liquid extraction or extractive or azeotropic distillation processes.

Introduction:

An alternative separation process is much to be desired to replace the more conventional azeotropic or extractive distillation used in the separation of closely boiling mixtures. There is a need to reduce both the energy costs associated with solvent recovery and costs due to loss of the expensive solvent. Ideally suited to the task would be a separating agent that could be readily flashed off, leaving a relatively pure product behind, assuring almost complete recovery of the solvent with a minimum expenditure of energy. Supercritical and near critical extraction where retrograde condensation and vaporization occur may be candidates for this task.

The separation of liquid mixtures by near critical solvents is still a relatively new technology. The lack of experimental phase equilibria data for many liquid systems and the dearth of solubility data for either critical gaseous solvents in liquid mixtures or for solutes dissolved in critical solvents makes any realistic design difficult. Some estimate can be obtained from an understanding of the general physical chemical principles involved, but ultimately each system must be addressed individually and its characteristics determined experimentally. In the discussion that follows, an experimental investigation was undertaken to determine the applicability of mixed solvents, near their critical conditions to the separation of butadiene from mixtures with 1-butene. These results are compared with predictions obtained from a representative equation of state in the region of the solvent-solute critical solution envelope.

Theoretical Discussion:

The recovery of butadiene from a mixed C₄ olefin stream has all of the characteristics of an energetically difficult separation resulting from the almost pinched VLE conditions existing in this mixture. As is shown in Table I, the physical properties of these components are almost identical with the exception of the large dipole moment of the 1-butene. Conventional distillation is impractical since the relative volatility of many of the C₄ compounds are reasonably close to unity. A separation, nevertheless, can be effected provided a suitably polar solvent is used to selectively remove the butene. The influence of polarity can be exploited in this separation by "salting out" the more nonpolar compound(1).

As a result, virtually all industrial practice for the recovery of butadiene currently makes use of extractive distillation with an entrainer such as acetonitrile or some other strong organic base to enhance the relative volatility of the components. The potential of achieving an equally effective separation through the introduction of a mixture of a solvent and an entrainer exhibiting polar properties close to its critical solution conditions is intriguing. Ammonia, a polar gas, has already been shown to act as an effective solvent(2) for this separation although at pressures much below its critical. Its use as a supercritical solvent for this separation would be also feasible were it not for its very high critical temperature (405.45 K) which favors the polymerization of the butadiene. A method developed in this work and described in a recent publication (3) makes use of a supercritical mixture of solvents which in combination provides the chemical as well as the physical conditions for the most efficient extraction of the 1-butene solute in the mixture within the limitations imposed by the thermal stability of the system.

The ability to effect the separation of various liquid solutions in the presence of a supercritical or near critical component has been adequately demonstrated(4). In general, these solvents tend to be either inorganic gases or light hydrocarbons such as carbon dioxide, ammonia, ethane, ethylene, or propane. For example, Weinstock and Elgin (5) used pressurized ethylene to promote the separation a number of miscible aqueous-organic liquid mixtures. Through the introduction of a solvent at or near critical conditions one can effect separation by forming multiple phases. The distributed component may concentrate in either one of the newly created phases. More recently several practical processes have been developed that use carbon dioxide to efficiently dehydrate ethanol(6). Deashing and the physical separation of asphaltines by supercritical propane have been commercially developed(7). Starling et al recently applied this concept to the separation of light hydrocarbons such as n-butane and n-decane(8). The theory of separation of multicomponent mixtures by SC solvents is now of current research interest with several papers devoted to the application of concepts of continuous thermodynamics(9,10) to handle multicomponent mixtures as well.

Reid and others(11,12) have shown that supercritical solvents show varying degrees of selectivity towards a particular solute. This is not surprising since the same principle that applies in liquid solvent selection should apply in the case of SC solvents. Because of the limited number of SC solvents available, the application of SC extraction to a broad range of systems is very limited. One way of increasing the applicability of the technique is either to find ways of expanding the solvent category, which does not seem likely at this time, or to develop methods of modifying existing solvents. Since the maximum selectivity of the solvent occurs when its critical temperature matches the extraction temperature, a match between the solute and the SC solvent is not always possible with a single solvent.

To circumvent this difficulty, Brunner(13) introduced an entrainer whose function is to modify the chemical activity of the solute mixture sufficiently to enhance the separation. This was put to use in the extraction of triglycerides from a mixture of polyglycerides using carbon dioxide with acetone as an entrainer. The entrainer served as a source of hydrogen bonding to augment the separation of the desired component. The principle of the entrainer in improving separation has been widely known in liquid extraction processes and described by Treybal(14).

A ternary nonideal solution, for example, will generally exhibit a minimum in one of the pairs of activity coefficients. The addition of a second solvent, if properly selected, may further lower the activity coefficient of the solute and increase its concentration in a given phase(15). The addition of a second component to an SC solvent will result in configurational effects that enhance the extraction of a pure solid. It can be shown theoretically that a binary SC solvent at pressures close to the critical envelope will also have a strong influence on the solubility of the solid solute(16). How well this principle can be extrapolated to multicomponent solids or liquid systems is still to be determined.

In this study, we have measured the degree of extraction of butene from a binary mixture of butadiene/ butene with various solvents eg. ethane, carbon dioxide, ethylene, ammonia and ethylene and ammonia and ethane solvent mixtures in the region of critical solution pressure of the solvent mixture. The experimental results are then compared with the VLE calculations for this system using a newly developed corresponding states equation devised by Ely and Mansoori(17).

The primary features of the equation are a new generalization for the shape factors and the use of propane as its reference component. The equation allows for the inclusion of multicomponent mixtures. The model has been successfully used with non-polar compounds and for a small number of selected polar compounds. It correctly represents liquid-vapor phase relations in the region of the critical, but does not specify the formation of a second liquid phase. The mixing rules, defined as $a_{ij} = (a_{iix}a_{jjj})^{1/2} (1-k_{ij})$ and $b_{ij} = \{ (b_{iil}^{1/3} + b_{jjj}^{1/3}) / 2 \}^3$, are then adjusted to account for the enhanced polar contribution of ammonia-butene through the interaction parameters, k_{ij} , and b_{ij} . All other interaction coefficients were set to $k_{ij} = 0$ and $b_{ij} = 1$. It is recognized that such a simplified model is in serious error since the polar and hydrogen bonding contributions are ignored. Nevertheless, it does permit one to obtain a "ball park" estimate of the separation likelihood. The results of these VLE flash calculations are then compared with our experimental results.

Experimental

Near-critical extraction experiments were carried out in a one-liter, stirred, stainless steel Autoclave (MR #7331), rated at 5000 psig at 600 F. Phase separations were monitored through an attached 50 cc Jerguson sight gauge (rated at 5000 psig at 72 F) which also served as a level indicator. A complete schematic of the assembly is shown in Fig.1. The autoclave was maintained at constant temperature by means of an external heating tape and an internal cooling coil. Cooling was furnished by a circulating water Freon refrigeration unit. An Autoclave magnetic stirring unit powered by an air motor was used to ensure adequate mixing of the sample volume. All lines were heat traced with electrothermal heating tapes. The reactor was depressurized before each experiment by venting the system and then evacuating the chamber under reduced pressure to ensure the complete removal of residual mixture and air from the system. Filling of the vessel was accomplished through a feed port at the base of the reactor. The samples of the upper and lower phases was removed through small bore (1/8 ") tubing through the head of the reactor and at the bottom of the reactor. No provision was made to sample any second liquid phase that may appear during an experiment.

Volumetric measurements obtained from observations through the sight glass of the Jerguson gauge and were used to determine the the molar volume of all liquid components used to make up the charge. A calibrated platinum thermocouple was used to measure the temperature of the contents of the autoclave reactor. The pressure of the system and of each of the receiver vessels were measured with calibrated high pressure precision Bourdon tube gauges of appropriate range. The gauge glass window was calibrated to give a direct reading of the volumes of the liquids added. When ammonia was used in the solvent makeup, it was added to the contents before the addition of the pressurizing solvent gas.

Ammonia was fed through a second Whitey pump into a storage cylinder that could be independently cooled to ensure minimum vaporization of the ammonia before admitting it to the reactor. The ammonia was added under a slight helium pressure to minimize liquid vaporization at the surface and to allow for a measurement of a quiescent interface.

The solvent gases, ethylene, carbon dioxide, or ethane, were fed by a Haskel gas compressor, Model AG-62, a 25-l air driven compression pump with a maximum outlet pressure of 9000 psig. The quantity of these gases introduced into the autoclave was determined by measuring the weight change of the gas cylinder and separately by a measurement of the change of the liquid level resulting from gas dissolving in the liquid during pressurization. The difference between the liquid level and the total volume of the vessel was measured and the second phase volume determined.

Chemically pure grade butene and butadiene were supplied in cylinders by Matheson Co. and used as received without further purification. The hydrocarbons were fed to the reactor through an LP10 Whitey laboratory positive displacement pump. A 30-pound nitrogen head was added to each hydrocarbon cylinder to maintain adequate pumping efficiency.

Heating controls were manually adjusted and the temperatures were indicated on a 10- point Acromag. The heating zones of the reactor were controlled by three Eurotherm 103 with voltage controlled manually by Variacs. The remaining sections were heat traced with self-limiting autotrace heating tapes to prevent condensation in the lines.

Sample Analysis:

The contents of the reactor were sampled before and after the introduction of the solvent gas and entrainer by trapping approximately 1 cc of the mixture from the reactor volume in a precalibrated volume of sample line located between two high pressure valves, adjacent to the vessel. The volume of the sample withdrawn was sufficiently small to minimize any changes in the pressure of the main contents of the vessel. Once trapped, the high pressure sample was further expanded into a pre-evacuated 300 cc Hoke cylinder to about 5 atm. This volume of sample was again expanded into a final 70-cc Hoke cylinder to about 1 atm. Portions of this volume were introduced into the Valco valve located at the Varian 920 Gas Chromatograph. All sample loops were heat traced as well to prevent condensation in the lines. This procedure was followed in sampling the lower portion of the liquid phase as well. An additional sample port was installed in the low pressure cylinder for syringe sampling to provide an additional check on the accuracy of sampling procedures.

The pressure of the gas was slowly increased until the liquid interface disappeared, indicating the attainment of the critical region. The gas pressure was then reduced by slightly depressurizing the chamber until the interface just reappeared. It was established that this procedure permitted the contents to be within 2 to 3 psi below the region of the critical. After stirring for about five minutes, the system was allowed to equilibrate before vapor and liquid phases were sampled.

Samples withdrawn from the upper and lower sections of the reactor autoclave were analyzed in the G.C. using a thermoconductivity detector with a 20', 1/8" VZ-7 packed column with helium used as the carrier gas. The G.C. was run with the injector set at 115 C, the column oven temperature at 60 C, and the detector set at 115 C. Filament current to the detector was set at 150 ma.

Samples were injected into the column by an air-operated Valco valve, which was controlled by a timer- controlled solenoid. The detector output was integrated and a concentration analysis was performed by an Autolab System. A Leeds and Northrup recorder was used to monitor the condition changes, and peak shapes, and composition analysis. The larger volume of solvent to solute required a change in sensitivity to adequately monitor the butadiene and butene peaks. A typical record of the GC output is shown in Fig.2 and indicates the integrated values of the represented peaks of the solvent gas, and butene and butadiene. The equilibrium compositions for each run are obtained in this manner and with the initial mixture composition tie lines of the system can be generated. The entrainer-solvent gas are considered as a pseudosolvent of fixed composition. The results of the measurements obtained for the 8% ammonia/ethylene are represented in the ternary diagram in Fig.3. Butene is represented as the distributed component with the butadiene as the heavy component.

Results:

The ratio of the integrated peaks for butene(i) and butadiene(j) was used to determine the separation factor, B, where the separation factor is defined as

$$B = \frac{\{y_i/x_i\} \text{solvent phase}}{\{y_j/x_j\} \text{heavy phase}} \quad (1)$$

The results shown in Table II and III are representative of the data collected for the studies conducted with ethylene and ethylene/ammonia and ethane and ethane/ammonia solvent mixtures. Table IV shows some selected data for other solvents and solvent mixtures as well. The results of extraction conducted with pure ethylene, carbon dioxide, and ethane in all cases showed no evidence of appreciable separation. In each set of experiments with single solvents, the same ratio of butadiene to butene was obtained in both phases. The butadiene/butene mixture is distributed in each phase in amounts that are primarily a function of the extracting gas and the temperature and pressure of the system.

Runs were made with several mixtures of ammonia/ethylene and ammonia/ethane with varying concentrations of ammonia. For both of these mixtures a separation of the butadiene was achieved, but the effect of the ethylene as a preferred solvent is most pronounced. The butene appears to be concentrated in the vapor phase in agreement with the findings of the earlier pure ammonia study(2). A series of experiments were also conducted to determine the temperature and pressure conditions in which maximum separation could be attained. For the ethylene/ hydrocarbon/ 8 % ammonia mixtures, this was found to be at 20 C and 600 psia. The maximum occurs at a pressure below the critical solution temperature determined by Lentz(18) for the ethylene/ammonia binary (Fig.4). The experimental selectivity was observed to decrease with an increase in pressure with an accompanying increase in the loading in the solvent phase. The selectivity is also reduced as the temperature rises all other things being equal(Fig.5).

Discussion

The results obtained in this study are by no means comprehensive and cover only a narrow range of variables. However, they indicate the maximum effect of entrainer enhancement on the relative volatility of an otherwise close-boiling mixture through the addition of 8% ammonia/ethylene solvent mixture close to its critical solution conditions. The relatively large selectivity achieved of 1.4 to 1.8 is to be considered in light of the value obtained for pure liquid ammonia of 1.63 reported by Poffenberger(2). Moreover, it is shown that the use of a solvent and an entrainer solvent permits the separation to be effected at temperatures and pressures lower than would have been otherwise predicted had pure critical ammonia been used, a result also observed by Fong et al(19) in studies of mixed solvent extraction of coal. An explanation for the lower than expected pressure for the separation is the likely formation of a Class IV mixture according to Van Konynenburg(20). It has been observed in

several systems containing ammonia and aromatics that a second liquid phase is formed under lower pressures than expected if the mixture behaved as an ideal Class I system. The P-T projection for these classes of mixtures is shown in Fig.6. A lower critical solution temperature (LCST) and an upper critical solution temperature (UCST) are the boundaries for the VLL phases observed to be present in these experiments. The critical points are the values for the two pseudo-components. Despite the fact that these phase relations are similar to those observed for a number of binary mixtures, one can consider the present mixture as a pseudo-binary system in which the solvent mixture, comprising ammonia and excess ethylene/ or ethane and a hydrocarbon phase of butadiene and butene exhibiting very similar vapor pressures.

The enhanced solubility of the solvent in the solution phase is evidenced in Table II by the large concentration of the ethylene present in both phases. An estimate of the volume of solvent added to the hydrocarbon mixture was obtained by calculating the difference in the liquid level before and after gas solvent addition. This is approximately the volume of gas dissolved in the liquid phase. This value is added to the volume above the liquid interface to obtain the total solvent added to the system. The volume of ethylene/ammonia solvent mixture added to the volume of butadiene/butene solution was approximately 5:1.

A comparison of the calculated selectivities obtained for the ethylene mixtures given in Table II can be made with the results in Table III obtained for the ethane system. These differences cannot be explained solely in terms of the critical properties of the respective gases. Usually the efficiency of extraction of a given solvent towards a particular solute is related to the proximity of the extraction temperature to the critical temperature of the solvent. The ratio of the two temperatures, T_{ext}/T_c , or the effective reduced temperature should be unity or somewhat greater to maximize separation. For a gas of given critical temperature, the reduced temperature is inversely proportional to the solubility of the solute in the solvent. Since ethane has a reduced temperature more nearly equal to unity at the extraction conditions at 20 C ($T_r = .98$) as compared with ethylene ($T_r = 1.47$), one would expect the ethane mixtures to be a better solvent for the butene. That this is not the case suggests an alternative explanation would be that the ethylenic double bond structure has a greater chemical affinity for the olefins in the solution phase which may account for the enhanced solubility of the butene in the ethylene phase. This is in addition to the chemical synergistic effect exerted by the ammonia which further increases the solubility of the butene in the vapor phase.

These results are also compared with calculated values obtained from the equation of state using $k_{ij} = 0.8$. Solvent to feed ratios as well as the effect of ammonia concentration in the solvent were independently varied to match the experimental data. The effect increasing ammonia concentration at constant pressure and temperature in both ethylene/ammonia and ethane/ammonia solvent mixtures are shown in Table V. The separation factor increases proportionally to an increase in entrainer concentration and appears to have a more important influence than either temperature or pressure. This is in contrast to the experimental observations in which the selectivity achieves a maximum at an ammonia composition of 8%. A comparison of these experimental findings with both the predictions of the present model and the Prausnitz model for the solubility of solute in mixed SC solvents suggests that chemical factors such as synergistic effects cannot be ignored and are likely to have a greater effect than anticipated. The vapor liquid equilibrium predictions are, in general, in fair agreement with the results of these experiments.

Conclusions:

1. The information presented in this study indicates the degree of mixing critical solvents with an appropriate component whose hydrogen bonding or polarity will enhance the separation of a close boiling mixture of butene-butadiene.
2. A maximum value in the selectivity of 1.4 - 1.8 can be achieved with a 5 - 8% ammonia concentration in ethylene for the butadiene - butene separation. This is in agreement with the predictions of the Ely-Mansoori equation of state. However, the presence of a maximum in the selectivity is not predicted by the model, suggesting the synergistic effect of the ammonia in the solvent rather than a concentration effect which is proportional to the added entrainer.
3. Ethylene/ammonia mixtures are more effective solvents for the separation of this mixture than is ethane/ammonia mixture with the same concentration of ammonia. It is suggested that ethylene because of its greater chemical similarity in the butene/butadiene solution exerts a greater influence on the binary activity coefficients of the system.

TABLE I
PROPERTIES OF C4 COMPONENTS

PROPERTY	1-BUTENE	1,3-BUTADIENE
Molecular Wt.	56.11	54.09
Critical Temp, C	146.4	152.20
Critical Press.MPa	4.019	4.329
Critical Vol. cc/mole	4.276	4.083
Normal BP,C	-6.25	-4.411
Solubility Param.	4.7504xE04	4.8694xE04
Dipole Mom. Debye	0.34	0.0
Acentric Factor	0.1867	0.1932

PROPERTIES OF SOLVENTS

PROPERTY	ETHANE	ETHYLENE	CARBON DIOXIDE	AMMONIA
Molecular Wt.	30.07	28.05	44.01	17.03
Critical Temp,C	32.27	9.21	31.04	132.50
Critical Press.				
MPa	4.88	5.03	7.38	11.27
Critical Vol. cc	4.919	4.601	2.136	4.255
Normal BP,C	-88.60	-103.7	-	-33.43
Solubility Coeff.				
	3.9134xE04	3.932xE04	4.605xE04	9.239xE04
Dipole Mom.Debye	0.0	0.0	0.0	1.47
Acentric Factor	0.09896	0.085	0.2276	0.2520

TABLE II

BUTADIENE-BUTENE-ETHYLENE-AMMONIA EQUILIBRIUM COMPOSITION

NH ₃ (%)	--- Solvent Phase (%) ---			---Butadiene Phase (%) ---			Beta
	C ₂ H ₄	Butene	Butadiene	C ₂ H ₄	Butene	Butadiene	
At T = 20° and P = 600 psia							
0	88.351	3.768	7.881	45.940	17.470	36.584	1.00
0	88.425	3.763	7.839	38.338	19.765	41.901	0.99
0	69.694	14.932	15.374	71.997	13.092	14.911	1.10
2.3	82.199	8.828	8.973	58.461	17.483	20.879	1.17
5.0	89.063	6.936	4.001	52.675	23.890	23.435	1.70
5.0	88.879	6.903	4.218	40.109	30.149	29.742	1.61
5.0	76.970	15.069	7.961	58.039	22.047	19.914	1.71
5.0	75.469	15.505	8.448	55.886	23.201	20.913	1.61
5.0	89.132	8.805	2.064	38.799	47.751	13.450	1.20
8.0	91.066	2.629	6.305	46.473	12.884	39.303	1.27
8.0	85.908	3.288	8.151	44.928	13.157	40.645	1.24
8.0	86.668	11.710	1.622	47.847	41.382	10.771	1.88
8.0	86.775	11.737	1.488	49.963	39.604	10.433	2.08
8.0	69.579	19.803	10.618	49.100	27.951	22.949	1.53
10.0	59.583	27.028	13.389	39.981	36.671	23.348	1.29
10.0	60.217	26.028	13.389	41.815	35.692	22.493	1.32
10.0	74.642	19.423	5.984	66.140	25.400	8.451	1.10
At T = 20°C and P = 800 psia							
2.3	70.166	13.873	15.960	34.716	28.791	36.493	1.10
2.3	69.498	14.112	16.389	43.984	24.539	31.477	1.10
5.0	76.947	12.740	10.312	74.065	14.520	11.415	1.05
5.0	77.599	12.566	9.835	74.093	14.494	11.413	1.00
10.0	81.026	7.044	11.930	67.741	11.236	21.021	1.10
10.0	80.266	3.354	12.183	67.009	11.767	21.224	1.12
At T = 20°C and P = 1100 psia							
0	69.694	14.932	15.374	71.997	13.092	14.911	0.90
0	81.759	8.583	8.713	73.607	12.124	14.270	0.86
5.0	84.760	8.380	6.860	77.316	11.457	11.227	0.84
5.0	84.074	8.457	7.451	74.816	12.849	12.335	0.92
At T = 40°C and P = 600 psia							
5.0	85.128	8.416	6.456	34.556	34.501	30.943	1.17
5.0	86.617	7.812	5.571	29.325	37.302	33.372	1.25
At T = 60°C and P = 600 psia							
5.0	75.099	11.814	8.756	19.215	42.621	38.163	1.21
5.0	74.163	12.412	9.471	20.693	41.856	37.451	1.17

TABLE III

BUTADIENE-BUTENE-ETHANE-AMMONIA COMPOSITION

EXPERIMENTAL VALUES

TEMP C	PRESSURE PSIA	NH3 %	SOLVENT PHASE			BUTADIENE PHASE			SELECTIVITY B
			C2H6 yi	BUTENE yj	BUTADIENE yk	C2H6 xi	BUTENE xj	BUTADIENE xk	
20	900	4.18	76.258	10.925	12.817	74.367	11.568	14.065	1.0
		4.18	76.505	10.834	12.661	74.993	12.079	12.929	1.09
		4.18	74.654	11.232	14.113	75.137	12.667	12.169	1.31
17	620	6.97	90.406	3.998	5.596	85.647	5.830	8.523	1.04
	640	6.97	90.107	4.123	5.770	83.324	6.804	9.871	1.03
	725	6.97	87.224	5.220	7.556	88.497	4.817	6.686	1.00
	725	6.97	87.387	5.181	7.432	88.766	4.497	6.737	1.05
	1060	6.97	88.840	4.489	6.689	93.178	2.751	4.071	1.00
	1060	6.97	88.90	4.443	6.657	93.086	2.801	4.113	1.00
19	675	6.97	85.525	7.426	7.229	88.073	6.047	5.879	1.00
	675	6.97	86.137	7.105	6.758	87.789	6.295	5.914	1.00
18	600	6.97	88.024	6.135	5.841	85.503	7.379	7.117	1.01
	600	6.97	87.722	6.201	6.077	85.812	7.185	7.002	1.00
16	550	6.97	95.867	2.252	1.977	76.208	11.624	12.168	1.19
18	600	6.97	83.134	10.507	6.358	80.277	11.959	7.577	1.05
20	600	6.97	82.572	10.834	6.594	80.176	12.228	6.044	1.02
	700	6.97	87.532	7.907	4.561	84.122	9.834	6.044	1.06
	700	6.97	87.295	8.009	4.696	83.794	10.026	6.180	1.05
22	525	1.85	89.169	5.166	5.664	69.808	15.252	14.939	1.0
	525	1.85	93.286	3.828	2.886	67.462	16.489	16.049	1.28
	525	1.85	92.362	3.900	3.737	78.235	11.064	10.701	1.01
	1100	1.85	88.100	6.345	5.555	78.508	11.205	10.288	1.04
	1100	1.85	87.700	6.328	5.973	78.581	11.078	10.341	1.00
23	550	0	82.754	8.164	3.668	53.113	22.449	24.438	1.00
	550	0	92.243	9.091	4.089	55.308	21.121	23.570	1.00
	1075	0	77.928	10.633	11.438	72.545	13.088	14.367	1.00
	1075	0	77.279	11.078	11.693	75.175	12.095	12.730	1.01

TABLE IV
SEPARATION OF EQUIMOLAR MIXTURES OF BUTENE-BUTADIENE
WITH VARIOUS SOLVENTS

EXPERIMENTAL VALUES			
TEMP. C	PRESSURE psia	SOLVENT	SELECTIVITY
6.0	750	C2H4	1.23
40.0	1100	CO2	1.0
22.0	1000	"	1.0
22.0	700	"	1.0
20.0	500	"	1.0
23.0	1100	C2H6/5% NH3	1.0
18.0	700	C2H6/7% NH3	1.06
20.0	900	C2H6/4% NH3	1.09
23.0	550	C2H6/	1.0

TABLE V
EFFECT OF TEMPERATURE AND PRESSURE ON THE SEPARATION OF EQUIMOLAR BUTENE
BUTADIENE SOLUTIONS USING NEAR CRITICAL AMMONIA-ETHYLENE MIXTURES
AS SOLVENTS

CALCULATED VALUES BY ELY-MANSOORI MODEL

$k_{ij}=0.8$, all others $k_{ij}=0$

MIXTURE COMPOSITION S/F		T	P	y	K	B
MOLE FRACTION		K	atm	butene	butene	

NH3/C2H4						
0.25	20	300	50	0.011	0.405	1.54
		310	50	0.0208	0.460	1.87
	10	300	50	0.0175	0.385	1.29
		305	50	0.024	0.393	1.37
		310	50	0.0317	0.407	1.40
0.50	10	320	50	0.0332	0.641	2.86
		330	50	0.426	0.786	3.10
		310	40	0.339	0.635	3.94
		320	40	0.433	0.834	4.29
NH3/C2H6						
0.50	10	320	40	0.0250	0.544	1.96
		330	50	0.0252	0.606	1.65
		350	58	0.0348	0.931	1.10
	20	315	40	0.0129	0.579	2.26
		320	40	0.0173	0.679	2.48
1.0	10	390	81	0.0331	0.900	0.91
		370	65	0.3636	0.512	1.13
0.0	2	295	20	0.5501	0.228	1.04

References:

1. Prausnitz, J.M., "Molecular Thermodynamics of Fluid Phase Equilibria", Chap. 10, Prentice Hall, N.Y. (1969)
2. Poffenberger, N., Horsley, L.H., Nutting, H.S., Trans. AIChE, 42, 815, (1946)
3. Joshi, D.K., Prausnitz, J.M., AIChE Jour. 30, 522, (1984)
4. Todd, D.B., Elgin, AIChE Jour. 1, 20, (1955)
5. Weinstock, J.J., Elgin, J.C., Jour Chem Engr. Data, 4, 3, (1959)
6. Fogel, W. Arlie, J.P., Revue Franc. Petrole, 39, 617, (1984)
7. Brule, M.R., Corbett, J.C., Hydrocarbon Process. 73, (1984) June
8. Starling, K.E., Khan, M.A., Watanasiri, S., Fundamental Thermodynamics of Supercritical Extraction, Presented Annual Mtg AIChE, San Francisco, Ca. (1984)
9. Prausnitz, J.M., Fluid Phase Equil., 14, 1, (1983)
10. Cotterman, R.L., Dimitrelis, D., Prausnitz, J.M., Ber. Bunsen Gesell. Phys. Chem., 9, 796, (1984)
11. Reid, R.C., Schmitt, N.J., The Influence of Solvent Gas on the Solubility and Selectivity in SC Extraction, Presented Annual Mtg AIChE., San Francisco (1984)
12. Vasilakos, N.P., Dobbs, J.M., Parisi, A.S., IEC Process Design, 24, 121, (1985)
13. Brunner, G., Fluid Phase Equil., Part II, 10, 289, (1983)
14. Treybal, R.E., "Liquid Extraction" 2nd Ed. McGraw-Hill, N.Y. (1963)
15. Prigogine, I., Bull. Soc. Chim. Belg., 52, 115, (1943)
16. Eckert, C.A., Greiger, R.A., IEC Process Design, 6, 250, (1967)
17. Mansoori, G.A., Ely, J.F., Density Expansion Mixing Rules, Unpublished (1984)
18. Lentz, H., Franck, E.U., Extraction by SC Gases, Ed. Schneider, G.M. Verlag Chemie, (1980)
19. Fong, W.S., et al., Experimental Observations on Systematic Approach to SC Extraction of Coal, Presented at National Mtg AIChE, New Orleans, La. (1981)
20. Van Konynenburg, P.H., Scott, R.L., Phil. Trans., Royal Soc., 298, 495, (1980)

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EXPERIMENTAL APPARATUS FOR THE MEASUREMENT OF BUTENE - BUTADIENE
SUPERCRITICAL EXTRACTION WITH SOLVENT GASES.

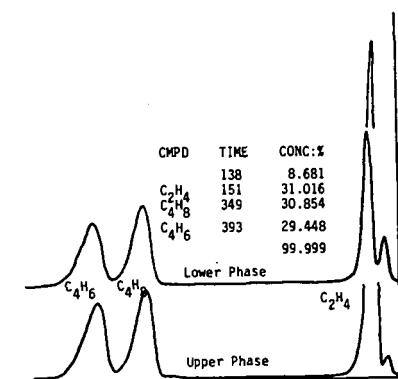
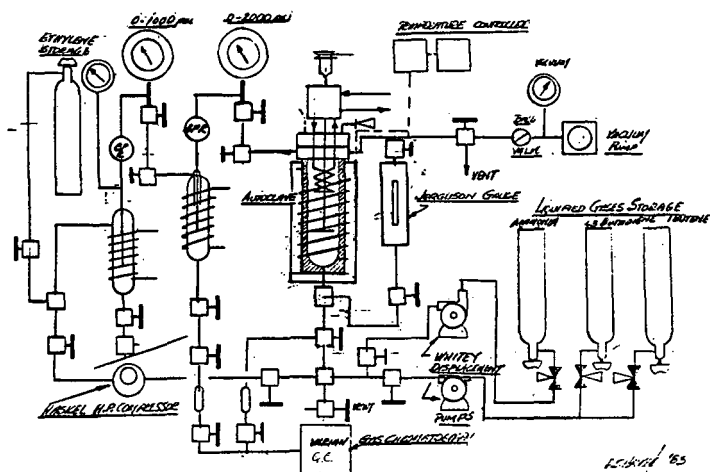


Figure 3. Ternary Phase Equilibrium for the System Butadiene - Butene with a Supercritical Solvent Mixture Ethylene - 8% Ammonia at 600 psi and 20°C. Experimental Points (•).

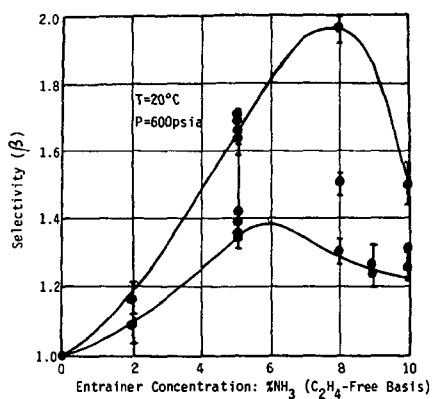


Figure 4. Influence of Entrainer Concentration on the Effectiveness of Solvent Ethylene.

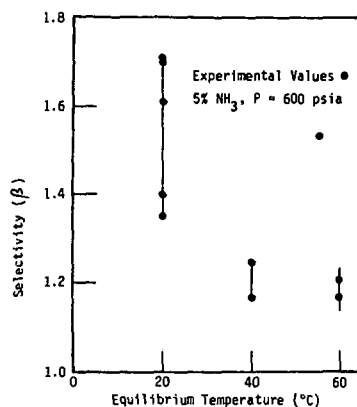


Figure 5. The Influence of Temperature on the Selectivity of Ethylene/Ammonia Solvent Mixtures on the Separation of C_4 Hydrocarbons.

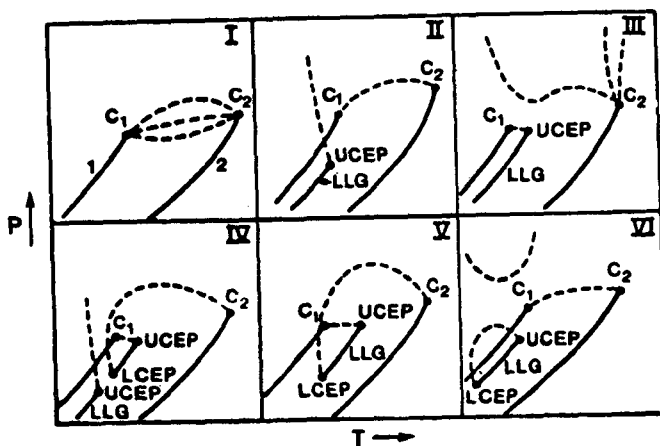


Figure 6. Classes of Different Binary Mixture Fluid Phase Behavior.